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Air Quality in Mecca and Surrounding Holy Places in Saudi Arabia During Hajj: Initial Survey

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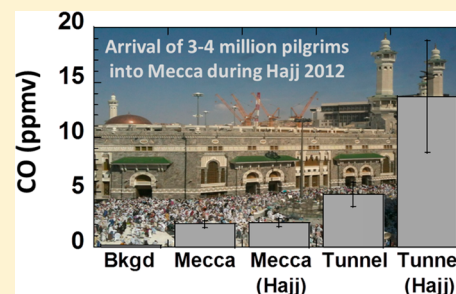
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Supporting Information

ABSTRACT: The Arabian Peninsula experiences severe air pollution, the extent and sources of which are poorly documented. Each year in Saudi Arabia this situation is intensified during Hajj, the Holy Pilgrimage of Islam that draws millions of pilgrims to Mecca. An initial study of air quality in Mecca and surrounding holy sites during the 2012 Hajj (October 24–27) revealed strongly elevated levels of the combustion tracer carbon monoxide (CO, up to 57 ppmv) and volatile organic compounds (VOCs) along the pilgrimage route—especially in the tunnels of Mecca—that are a concern for human health. The most abundant VOC was the gasoline evaporation tracer *i*-pentane, which exceeded 1200 ppbv in the tunnels. Even though VOC concentrations were generally lower during a follow-up non-Hajj sampling period (April 2013), many were still comparable to other large cities suffering from poor air quality. Major VOC sources during the 2012 Hajj study included vehicular exhaust, gasoline evaporation, liquefied petroleum gas, and air conditioners. Of the measured compounds, reactive alkenes and CO showed the strongest potential to form ground-level ozone. Because the number of pilgrims is expected to increase in the future, we present emission reduction strategies to target both combustive and evaporative fossil fuel sources.



INTRODUCTION

In many urbanized areas, traffic emissions are the principal local source of air pollutants such as volatile organic compounds (VOCs) and carbon monoxide (CO),^{1,2} though natural gas, liquefied petroleum gas (LPG), local biomass incineration and industrial emissions can also be significant contributors.^{3–6} Natural gas is primarily composed of methane (CH₄), while liquefied petroleum gas is primarily propane and the butanes.^{3,5} Combustive traffic emissions include CO, ethyne, and ethene, while gasoline evaporation is characterized by *i*-pentane. Isoprene is a characteristic biogenic emission tracer, though it also has a vehicular source.^{7,8}

In addition to contributing to high ozone (O₃) levels and photochemical smog, many of these air pollutants have adverse health effects in both the short- and long-term.^{9–13} For example benzene is a known carcinogen that causes leukemia,^{12,13} and elevated CO levels have recently been shown to increase the risk of heart failure.¹¹ The World Health Organization estimates that air pollution is responsible for over a million premature deaths worldwide every year¹⁴ and has recently classified outdoor air pollution as a human carcinogen.¹⁵ Other compounds such as long-lived halocarbons have negligible sinks in the troposphere and instead break down in the stratosphere,

where their byproducts are harmful to the protective stratospheric O₃ layer.¹⁶

Urban populations and traffic continue to grow despite increasing congestion and pollution. The Holy City of Mecca in the Kingdom of Saudi Arabia (21°25'N, 39°49'E) is located 80 km from the Red Sea in a valley with mountains to the north and south (Supporting Information (SI) Figure S1). The population of Mecca has sharply increased from 366 000 in 1974 to 1.67 million today.¹⁷ Uniquely to Mecca, more than 15 million Muslim pilgrims visit each year, including 3–4 million during Hajj, the Holy Pilgrimage of Islam. The Hajj pilgrimage route leads from Al-Masjid Al-Haram, the world's largest mosque (also called the Grand Mosque) to Mount Arafat approximately 20 km to the east (Figure 1).

Mecca is still expanding and the number of Hajj pilgrims is expected to rise to 4–5 million by 2020.¹⁸ Therefore, the peak seasons of Hajj and Ramadan (the month of fasting) represent major tests to the local infrastructure. To handle the crowds of

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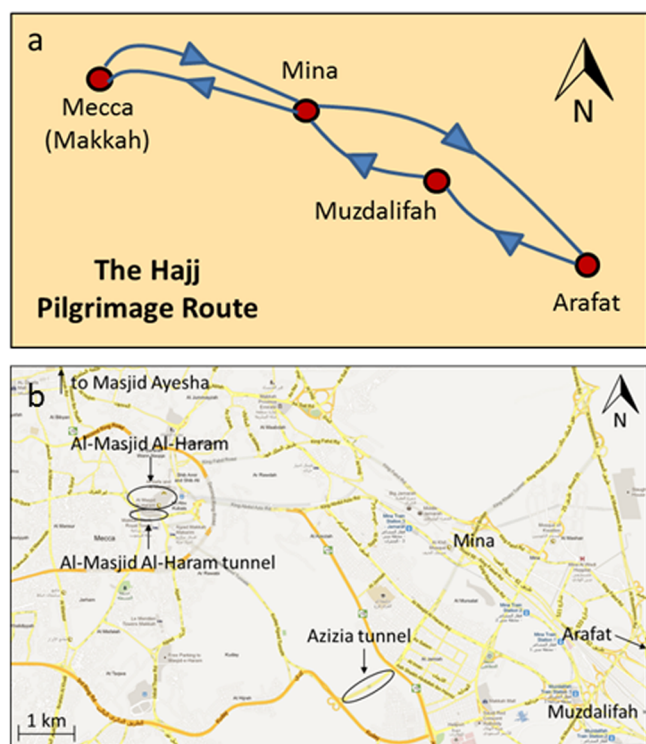


Figure 1. (a) Overview of the Hajj pilgrimage route. (b) Details of Mecca (Makkah) including locations of Al-Masjid Al-Haram (the Grand Mosque) and two tunnels that were sampled. On October 24, 2012 the pilgrims traveled from Al-Masjid Al-Haram (the Grand Mosque) to Mina where they spent the night. On October 25 they continued to Arafat and spent the night in Muzdalifah. On October 26 they traveled to Mina and spent the night. After stoning the jaramāt (walls), the pilgrims returned to the Grand Mosque in Mecca on October 27.

pilgrims and allow them to move among the different holy sites, the Saudi government has an ongoing program to construct more roads and tunnels through and around Mecca's mountains. The current network of tunnels connects the old city of Mecca to new districts and includes vehicle-only, vehicle-and-pedestrian, and pedestrian-only tunnels. However, crowding during Hajj and Ramadan causes the traffic to slow in the tunnels, sometimes coming to a complete stand-still. Even though tunnel ventilation systems operate at maximum capacity, the high volume of traffic and limited capacity of the tunnels means that poor air quality is a concern to tunnel users and local residents.

The Arabian Peninsula already experiences severe O_3 pollution and photochemical smog, with year-round exceedances of European air quality standards.¹⁹ Despite this, Saudi Arabia and the surrounding region is a highly understudied region in terms of ground-based measurements of O_3 and its precursors.^{19,20} Here we present results from an initial ground-based survey of air quality in western Saudi Arabia, focusing on air quality and human health impacts associated with the arrival of 3–4 million pilgrims into the Mecca area during Hajj 2012 (October 24–27, 2012 or 8–11 Dhul-Hijjah 1433H). The measurement campaign targeted carbon dioxide (CO_2), CH_4 , CO and 96 speciated C_1 – C_{10} VOCs. The first day of arrival into Saudi Arabia for pilgrims was September 17, 2012 and the final day of departure was November 29, 2012.

MATERIALS AND METHODS

Air Sampling. Ground-level air samples were collected in Mecca and surrounding holy sites between October 18 and November 1, 2012 during the season of Hajj ($n = 72$) and again from April 7–12, 2013 ($n = 44$) (SI Table S1). Each air sample was collected into a conditioned and evacuated 2 L stainless steel canister fabricated specifically for our group. Each canister has a bellows valve, and the person collecting the sample manually opened the valve until the canister was filled to ambient pressure. This took approximately 1 min, at which time the valve was tightly closed. The sampling focused on Mecca and the main Hajj pilgrimage route, which extends 20 km to the east and includes Mina, Arafat and Muzdalifah (Figure 1 and SI Figure S1). The 2012 Hajj journey (in vehicles) started at noon on October 24 with pilgrims moving from Mecca to Mina (a 5 km distance) where they spent the remainder of the day and part of the night in centrally air conditioned tents, with about 40 people per tent. From Mina, pilgrims got ready at midnight and arrived in Arafat early in the morning of October 25. After sunset, pilgrims left Arafat for Muzdalifah where they spent the night under the open sky; this is the busiest time for overcrowding and heavy vehicular traffic. The pilgrims spent the following night (October 26–27) in the tents in Mina before returning to Mecca. The air sampling along the pilgrimage route focused on these periods of maximum activity (SI Table S1). An additional 40 air samples were collected elsewhere in western Saudi Arabia from October 18 to November 13, including Jeddah and Medina, which were more representative of the larger area (SI Figure S1). Because the Mecca air samples were heavily impacted by Hajj activities, averages from the lowest 10th percentile of data for each compound ($n = 13$) from the combined Mecca and regional study ($n = 112$) were used here to help assess local/regional background concentrations (see SI).

The Mecca sampling during Hajj also included two tunnels: the Al-Masjid Al-Haram or Souq al-Sagheer tunnel ($n = 7$) and the King Khalid Tunnel-1 or Azizia tunnel ($n = 6$) (Figure 1b). The 750 m Al-Masjid Al-Haram tunnel is a six-lane vehicle-and-pedestrian tunnel that leads to the Grand Mosque and is busy year-round. During Hajj 2012 vehicle speed in the tunnel slowed from 20 to 30 km/h to 0–5 km/h, with traffic jams of up to an hour. Many police and volunteer workers stayed inside the tunnel to control and direct vehicles and pilgrims. The tunnel also serves as a passage into a 7-star hotel through its basement, and workers and security personnel remain in the tunnel for 6–8 h shifts. One-minute integrated air samples were taken after walking into the middle of the tunnel. The 922 m Azizia tunnel is a six-lane vehicle-only tunnel that connects surrounding districts to Mecca and is also busy year-round. During Hajj the vehicle speed slowed from 80 to 100 km/h to 5–10 km/h and traffic was sometimes stuck for 20–30 min. Most vehicles driving in the tunnel have closed windows, but open vehicles and (more rarely) motorbikes are also used. Vehicles without air conditioning systems may also drive with open windows. One-minute integrated samples were collected in the middle of the tunnel from outside a car window. These two tunnels were resampled in April 2013 when Hajj was not occurring ($n = 4$ at each tunnel).

Laboratory Analysis. The samples were returned to the University of California, Irvine (UC Irvine) via commercial courier and analyzed using multicolumn gas chromatography (GC) with flame ionization detection (FID), electron capture

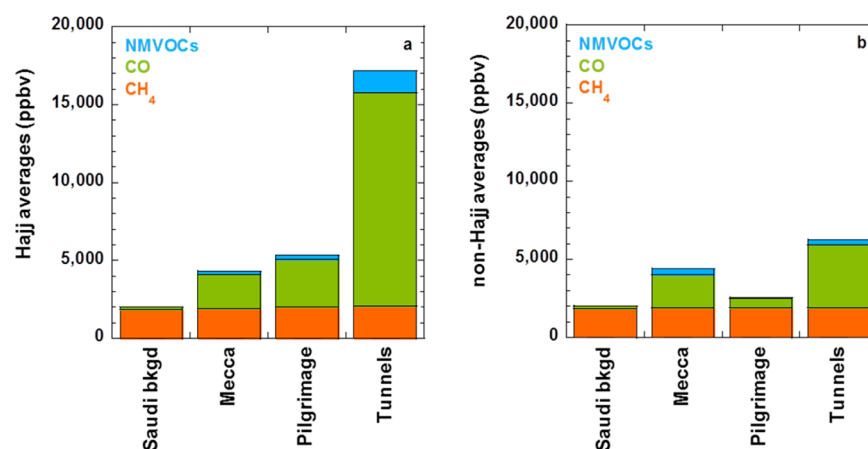


Figure 2. Average mixing ratios of methane (CH_4 , orange), carbon monoxide (CO, green), and total measured nonmethane VOCs (NMVOCs, blue) during (a) the season of Hajj from October 18 to November 1, 2012, and (b) April 7–12, 2013 when Hajj was not occurring. “Saudi bkgd.” = lowest 10th percentile from a larger regional study conducted during each campaign (see text and SI Figure S1). The dates of sample collection and number of samples per site are shown in SI Table S1.

detection (ECD) and mass spectrometer detection (MSD).²¹ This ultrasensitive measurement technique was used to accurately identify and precisely quantify 96 different C_1 – C_{10} VOCs (SI Table S2). Carbon dioxide, CH_4 and CO were analyzed separately using GC with a thermal conductivity detector (TCD) for CO_2 and GC/FID for CO and CH_4 . Details are given in the SI.

The VOC mixing ratios covered a large range, from subparts per trillion by volume (pptv, 10^{-12}) to parts per million by volume (ppmv, 10^{-6}). Our calibration procedure uses multiple standards, including working standards that are analyzed every four samples and absolute standards that are analyzed twice daily.²¹ UC Irvine has participated in every formal international VOC intercomparison experiment and we regularly participate in informal intercomparisons, with excellent results.^{22–24} The precision, accuracy and detection limit for each VOC is listed in SI Table S2. The target VOCs presented here are stable in our canisters to within the stated uncertainties for several months (see SI).

RESULTS AND DISCUSSION

General Features during Hajj 2012. Very high levels of CO and nonmethane VOCs (NMVOCs) were measured during the 2012 Hajj (SI Table S2; Figure 2a). The discussions below address CO, CH_4 , and NMVOCs, and the uncertainties represent one standard error. Methane was the most abundant measured component in the lowest 10th percentile of data ($n = 13$)—hereinafter referred to as the Saudi regional background—with comparatively small amounts of CO and NMVOCs (Figure 2a). By contrast, the most polluted air during Hajj 2012 was measured in the tunnels of Mecca ($n = 13$), and its predominant component was the combustion tracer CO (Figure 2a). The gasoline evaporation tracer *i*-pentane was the most abundant NMVOC measured during Hajj, reaching over 1200 ppbv in the Al-Masjid Al-Haram tunnel compared to a regional background of 0.74 ± 0.15 ppbv (SI Table S2). In between these two pollution extremes were urban air in Mecca ($n = 49$) and air along the pilgrimage route in Mina, Arafat and Muzdalifah ($n = 10$). As in the tunnels, CO was the most abundant compound measured in Mecca and along the pilgrimage route (Figure 2a). The different air sampling groups are discussed in more detail below.

1. “Background” Air. The concentration of CH_4 in the Saudi regional background was the same as in background air measured at a similar time and latitude in the remote Pacific Basin as part of UC Irvine’s long-term global trace gas monitoring program (September 2012, 20 – 23°N ; ²⁵) (SI Table S2). By contrast, CO concentrations in the Saudi regional background were roughly double that in the Pacific basin background, and summed NMVOCs were roughly triple (SI Table S2). Notably elevated NMVOCs in the Saudi background included the C_4 – C_6 alkanes, benzene, toluene, and ethene. Overall the higher background levels of CO and several VOCs in western Saudi Arabia compared to the remote Pacific is consistent with the presence of regional air pollution in the Arabian Peninsula.¹⁹

2. Mecca. The nontunnel urban Mecca samples during Hajj were clearly more polluted than the Saudi regional background (SI Table S2). Methane levels were 55 ppbv higher in Mecca than in the Saudi regional background; NMVOC levels were 20 times higher in Mecca compared to background; and CO levels increased from 170 ± 13 ppb in background air to 2230 ± 380 ppbv in Mecca (SI Table S2). For example, very high CO levels (1430–7830 ppbv) were measured at Masjid Ayesha ($n = 6$), an important worship place about 8 km northwest of the Grand Mosque (Figure 1b) where frequent visits during Hajj and on regular days increase the traffic load. The butanes and pentanes all reached their highest nontunnel values near Masjid Ayesha (e.g., over 800 ppbv for *i*-pentane). *i*-Butane, *n*-butane, and *n*-pentane all correlated much better with the gasoline evaporation tracer *i*-pentane ($R^2 = 0.92$ – 1.00) than with the combustion tracer CO ($R^2 = 0.13$ – 0.18) (SI Figure S5a,b). Together the CO and C_4 – C_5 alkane enhancements indicate the strong presence of both combustive and evaporative fossil fuel sources at Masjid Ayesha.

Like CO, the combustion tracers ethyne and ethene were also abundant in Mecca, exceeding their respective background values by more than a factor of 25 (SI Table S2). Levels of some halocarbons were also elevated in Mecca. Average levels of the CFC-replacement compounds HCFC-22, HCFC-141b, and HCFC-142b were 2.0–2.6 times larger than in the regional background, and average levels of HFC-134a, a refrigerant and automobile air conditioner, were 5.5 times larger (SI Table S2).

3. The Pilgrimage Route. In addition to tracers of vehicular exhaust and gasoline evaporation such as CO, benzene and *i*-pentane (Figure 3a–c), remarkably elevated levels of HCFCs

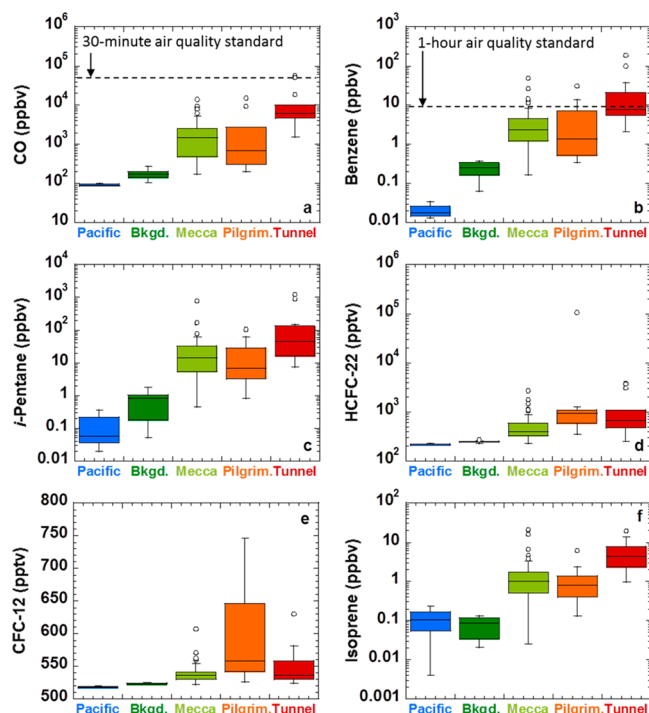


Figure 3. Box-whisker plots of (a) carbon monoxide, (b) benzene, (c) *i*-pentane, (d) HCFC-22, (e) CFC-12 and (f) isoprene mixing ratios in western Saudi Arabia during Hajj 2012. “Outliers” (open circles) are values greater than the third quartile plus 1.5 times the interquartile distance. Background air samples collected in the remote Pacific basin at Mecca latitudes in September 2012 are also shown for comparison (blue; $n = 4$). Green: Saudi regional background ($n = 13$); light green: nontunnel air in Mecca ($n = 49$); orange: Hajj pilgrimage route samples in Mina, Arafat, and Muzdalifah ($n = 10$); red: Mecca tunnel samples ($n = 13$). Note the logarithmic y -axis scale for most panels. Units are ppbv, except HCFC-22 and CFC-12 which are pptv. The 30 min air quality standard for CO (50 ppmv) is from refs 24 and 25. The 1 h air quality standard for benzene (9 ppbv) is from refs 30 and 31.

and HFCs were also measured along the pilgrimage route during Hajj. The O_3 depletion potential of HCFCs is much lower than the CFCs that they replace, and HFCs do not destroy stratospheric O_3 . However, both HCFCs and HFCs are of concern because they are potent greenhouse gases.²⁶ The average mixing ratio of HFC-134a (4.4 ± 3.8 ppbv), a replacement for CFC-12 in domestic and mobile air conditioners, was 48 times larger along the pilgrimage route than in the regional background, though the pilgrimage average was driven by a maximum value of 38.7 ppbv (SI Table S2). The average level of HFC-152a (21.4 ± 21.3 ppbv), an alternative to HFC-134a in mobile air conditioners, was more than 2100 times larger than the regional background, though again driven by a maximum value of 213 ppbv. For both HFC-134a and HFC-152a, as well as many other halocarbons including HCFC-142b and HCFC-22 (Figure 3d), their maximum value was measured between Arafat and Muzdalifah at 8:20 p.m. on the peak night of October 25 when traffic was heavy and very slow-moving. This the busiest time of Hajj because all 3–4 million pilgrims want to move from Arafat to Muzdalifah at the same time, just after sunset.

In addition to CFC replacement compounds, CFCs were also elevated levels along the pilgrimage route (SI Table S2; Figure 3e). In particular, CFC-12 averaged 0.596 ± 0.026 ppbv along the pilgrimage route, with a maximum value of 0.746 ppbv on the evening of October 25, compared to a regional background of 0.523 ± 0.001 ppbv. This indicates ongoing emissions of this banned ozone-depleting compound and potent greenhouse gas.

The most polluted nontunnel air sample was measured along the pilgrimage route at the King Abdullah bridge in Mina on the morning of October 27, the final day of Hajj. During Hajj the bridge is used for pedestrians and diesel-powered buses, as well as gasoline-powered vehicles. The bridge also crosses over a road with gasoline-powered vehicles. During Hajj all vehicles were slow-moving and idling for hours. The very high CO level at this site (14 780 ppbv) indicates a major contribution from vehicle exhaust.

4. Tunnel Samples. Even though heavily polluted air was measured in Mecca and along the pilgrimage route, the most polluted air of the study was inside Mecca’s tunnels. Apart from CO_2 , the most abundant measured compounds in the tunnels were CO, *i*-pentane and ethyne, with respective average values of $13,700 \pm 5100$ ppbv, 208 ± 107 ppbv and 157 ± 61 ppbv (SI Table S2). The average CO level in the tunnels was more than 80 times higher than regional background (Figure 3a). The maximum CO level during Hajj (57 400 ppbv) was measured in the Al-Masjid Al-Haram tunnel at 4 p.m. on October 19 and is the highest CO level ever recorded by our group in an urban environment. Although this is only a 1 min integrated air sample (recommendations for expanded air monitoring in the tunnels are given below), it exceeded the 30 min exposure guideline of 50 000 ppbv.^{27,28} In addition to causing adverse effects including headaches, dizziness and nausea at levels of 35–800 ppmv, elevated CO levels increase the risk of heart failure hospitalizations or death by 3.5% for every ppmv over background.¹¹ Given the elevated CO levels observed in the Al-Masjid Al-Haram tunnel together with the exposure times experienced by motorists, pedestrians, police, volunteers, and others (see above), elevated risk of heart failure is a realistic concern.

Similarly, the average benzene level in the tunnels (32 ± 15 ppbv) was more than 130 times higher than the regional background (Figure 3b). Like CO, the maximum benzene level of the study (185 ppbv) was also measured in the Al-Masjid Al-Haram tunnel at 4 p.m. on October 19. Benzene has both acute health effects such as narcosis, and long-term health effects such as cancer. It is difficult to recommend an acute exposure limit for benzene. Recent literature suggests there is no safe exposure limit to benzene because it is a known carcinogen and does not appear to have a functional low dose threshold.^{13,29} Here we use a 1 h exposure limit of 9 ppbv.^{30,31} Again bearing in mind the 1 min sampling time, several benzene values exceeded the 1 h limit (Figure 3b), suggesting potential health concerns. Benzene specification levels are larger in Saudi Arabian gasoline than in many other locations around the world,³² which may be a factor in the high benzene levels measured in the tunnels.

Source Influences. Besides CH_4 , the top 30 most abundant VOCs during Hajj were C_4 – C_6 alkanes, ethyne, C_2 – C_5 alkenes, toluene, benzene, HFC-152a, and HCFC-22 (SI Table S2). These compounds are primarily associated with fossil fuel combustion and evaporation, LPG, and industry. The major sources of VOCs in western Saudi Arabia during Hajj were

investigated using a combination of VOC ratios and linear correlation analysis.

1. Vehicular Exhaust. The characteristic emission ratio of ethene/ethyne is 10–30 for petrochemical sources and 1–3 for vehicular exhaust, with older emissions control technology yielding lower ratios (1 or lower) due to higher ethyne emissions.^{33,34} During Hajj the ethene/ethyne ratio was 0.73 ± 0.06 in the urban Mecca samples ($R^2 = 0.76$), 0.85 ± 0.06 along the pilgrimage route ($R^2 = 0.96$) and 0.25 ± 0.02 in the tunnels ($R^2 = 0.93$), clearly showing the influence of vehicular rather than petrochemical sources and the lack of emission control technology in Mecca's vehicle fleet (SI Figure S2a). Benzene correlated well with the combustion tracer CO in the tunnels ($R^2 = 0.83$), indicating its vehicular rather than industrial influence (SI Figure S2b). However, benzene showed poorer correlation with CO in Mecca ($R^2 = 0.58$) and along the pilgrimage route ($R^2 = 0.59$), suggesting an additional noncombustive source such as industry. Consistent with this, benzene showed better correlation with the urban/industrial tracer C_2Cl_4 in Mecca ($R^2 = 0.66$) and along the pilgrimage route ($R^2 = 0.48$) than in the tunnels ($R^2 = 0.04$) (SI Figure S5c).

While isoprene's main source is biogenic, previous studies have also shown a vehicular source of isoprene.^{7,8} Here isoprene was strongly elevated above the regional background in urban areas of Mecca, along the pilgrimage route and in the tunnels (Figure 3f). For example its average tunnel value (6.0 ± 1.5 ppbv) was 80 times the regional background (SI Table S2). Isoprene showed some correlation with CO in Mecca and its tunnels ($R^2 = 0.56$ and 0.33 , respectively; SI Figure S5d), consistent with some contribution from vehicular sources. Isoprene reacts quickly with the hydroxyl radical (OH), O_3 and NO_3 . Poor correlation between isoprene and CO in tunnels has recently been explained by high levels of nitrogen oxides (NO_x) removing most of the O_3 sink together with lack of sunlight inhibiting OH production, making NO_3 the main sink and causing isoprene to be removed faster than CO and other VOCs.³⁵

2. Liquefied Petroleum Gas (LPG). The *i*-butane/*n*-butane ratio is 0.2–0.3 for vehicular exhaust, 0.42–0.46 for LPG and other fuel gases, and 0.6–1.0 for natural gas.^{19,36} Saudi Arabia produces 14% of the world's LPG³⁷ and LPG is used for domestic purposes within Saudi Arabia. During Hajj the *i*-butane/*n*-butane ratio was 0.44 ± 0.01 in Mecca ($R^2 = 0.99$), 0.32 ± 0.02 along the pilgrimage route ($R^2 = 0.97$) and 0.35 ± 0.03 in the tunnels ($R^2 = 0.94$) (SI Figure S2c). A strong natural gas influence was ruled out (see SI), and these slopes suggest a primary vehicular exhaust source along the pilgrimage route and in the tunnels, and a primary influence from LPG (or other fuel gases) in the urban Mecca samples, likely from domestic LPG use. However, this source assignment would benefit from collecting samples directly from LPG tanks and other fuel gases used in Mecca (i.e., source samples).

3. Gasoline Evaporation. *i*-Pentane is a characteristic tracer of gasoline evaporation. An *i*-pentane/*n*-pentane ratio near 3.8 indicates gasoline evaporation³⁸ while a value closer to 0.86 reflects natural gas.³⁹ The *i*-pentane/*n*-pentane ratio during Hajj was 3.52 ± 0.02 in Mecca ($R^2 = 1.00$), 2.93 ± 0.07 along the pilgrimage route ($R^2 = 1.00$) and 3.54 ± 0.04 in the tunnels ($R^2 = 1.00$) (SI Figure S2d), clearly showing the influence of gasoline vapors rather than natural gas. Within urban (nontunnel) areas of Mecca, the C_2 – C_3 alkenes correlated much better with CO ($R^2 = 0.72$ – 0.82) than with *i*-pentane (R^2

$= 0.02$ – 0.03), showing their primary combustion source (SI Figure S4a,c). Conversely, the C_4 – C_5 alkenes showed a stronger correlation with *i*-pentane ($R^2 = 0.81$ – 0.99) than with CO ($R^2 = 0.14$ – 0.47), indicating their primary evaporative source (SI Figure S4b,d). As in the case of LPG, direct gasoline vapor samples would allow this source to be more fully characterized.

4. Air Conditioners. Emissions of controlled CFC replacements, and to a lesser extent banned CFCs, were also observed during the Hajj study, especially along the pilgrimage route. CFC replacement compounds such as HCFCs are purely anthropogenic compounds that are used as refrigerants.^{40,41} They can leak from cooling appliances, which during this study were most likely stationary and mobile air conditioning units. During Hajj days, air conditioning in the buses that transport the pilgrims runs continuously, especially during traffic jams in tunnels and on roads. During both Hajj and non-Hajj days, window air conditioners are used in rooms throughout local residences. Also, as stated above, millions of pilgrims stay in air conditioned tents during their two overnight stays in Mina.

Overall, the Hajj 2012 VOC data show predominant influences of vehicular exhaust and gasoline evaporation in Mecca, the tunnels of Mecca and along the pilgrimage route. Emissions from LPG or fuel gas and air conditioning units were also clearly observed.

Potential for Ozone Formation. Although we did not measure O_3 directly during this initial study, many of the VOCs we quantified have significant potential to form ground-level O_3 through their reaction with OH, the primary oxidizing agent in the atmosphere. As a proxy for direct O_3 measurement, the hydroxyl radical reactivity (k_{OH}) quantifies the contribution that individual VOCs (and other species) make to O_3 formation.⁴² The more concentrated the VOC and the more reactive it is, the greater its potential to form tropospheric O_3 (see SI) During the Hajj study, CO and 77 of the measured VOCs were used to calculate k_{OH} (see SI Table S2). The k_{OH} values varied widely, from $2.5\ s^{-1}$ in regional background air, to $90\ s^{-1}$ in Mecca, $91\ s^{-1}$ along the pilgrimage route, and $591\ s^{-1}$ in the tunnels (Figure 4). That is, only the regional background was comparable to “clean air” values of 1 – $3\ s^{-1}$, while k_{OH} in urban spaces of Mecca was similar to the world's major cities (10 – $100\ s^{-1}$).^{43,44} Because other O_3 precursors such as NO_x were not taken into account here, the k_{OH} values are likely to be low

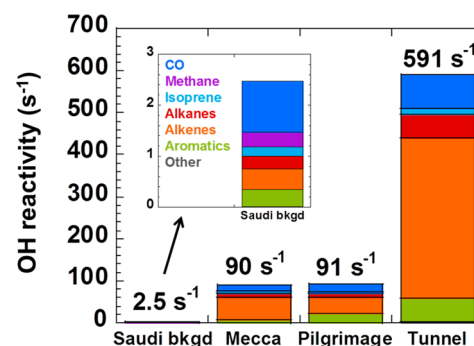


Figure 4. Contributions of CO and 77 VOCs to OH reactivity (k_{OH}) during Hajj 2012. “Bkgd”: Saudi regional background; “Mecca”: nontunnel urban air in Mecca; “Pilgrimage”: air samples along the Pilgrimage route; “tunnel”: air samples from the Al-Masjid Al-Haram and Azizia tunnels in Mecca. Sampling dates and numbers are given in SI Table S1. Inset: “Bkgd” detail.

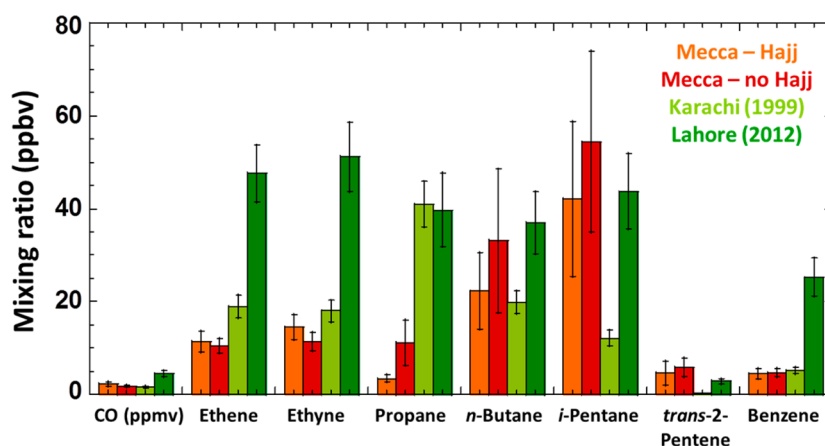


Figure 5. Average mixing ratios of selected VOCs in urban areas of Saudi Arabia and Pakistan. Orange: Mecca during Hajj 2012; red: Mecca in April 2013 when Hajj was not occurring; light green: Karachi in January 1999; green: Lahore in December 2012. Units are ppbv, except CO which is ppmv. Uncertainties represent ± 1 standard error.

estimates. Even so, they already show the clear potential for strong O_3 formation in the Mecca area.

Carbon monoxide, CH_4 and isoprene were the strongest individual contributors to O_3 formation in the regional background air, comprising 41%, 12%, and 7% of k_{OH} , respectively (Figure 4). Alkenes became increasingly responsible for k_{OH} as the air progressed from clean to polluted. Excluding isoprene, which has both biogenic and anthropogenic sources, the alkene contribution to k_{OH} increased from 10% for regional background air, to 43% along the pilgrimage route, 59% in Mecca, and 65% in the tunnels. The top individual contributors to k_{OH} in Mecca during Hajj 2012 were CO (15%), *i*-butene (9%) and *trans*-2-pentene (8%). Whereas CO is a combustion product associated with vehicular exhaust, the C_4 – C_5 alkenes were attributed primarily to an evaporative rather than combustive fossil fuel source (see above). This finding has important implications for choosing the best strategy to control O_3 formation in the Mecca area. Specifically, efforts to curb O_3 require dual targeting of both CO and alkenes via coordinated efforts to reduce trace gas emissions from both combustive and evaporative fossil fuel sources.

Comparison with Non-Hajj and Literature. The VOC levels during Hajj 2012 were compared with those collected in April 2013 when Hajj was not occurring. The respective concentrations of CO, CH_4 and NMVOCs were similar during the Hajj 2012 and April 2013 studies both for Saudi background air and for nontunnel areas of Mecca (Figure 2). For example, the average CO level in urban Mecca was 2230 ± 380 ppbv and 2095 ± 420 ppbv during Hajj 2012 and April 2013, respectively. Instead, the key changes in April 2013 compared to Hajj 2012 were lower CO and VOC levels along the pilgrimage route (especially Mina and Muzdalifah) and less air pollution in the Al-Masjid Al-Haram and Azizia tunnels in Mecca (Figure 2). For example, the average CO level measured along the pilgrimage route was 3040 ± 1580 ppbv during Hajj compared to 620 ± 410 ppbv in April 2013. Respective average levels of CO, *i*-pentane and ethyne—which were the most abundant compounds in the tunnels during Hajj—were 2.2–4.9 times higher during Hajj ($13,700 \pm 5100$ ppbv, 208 ± 107 ppbv and 157 ± 61 ppbv) than in April 2013 (4830 ± 1120 ppbv, 95 ± 62 ppbv, and 32 ± 9 ppbv), showing the strong additional impact of vehicular emissions on air quality in Mecca's tunnels during Hajj. By comparison, the average CO

level in Mecca's tunnels during Hajj was similar to that in the Hsuehshan Tunnel in Taiwan in July–August 2006, based on the average of hourly CO concentrations at four monitoring sites in the tunnel (9900 ± 1700 ppbv;⁴⁵) and to the Thiais tunnel in Paris in August 1996 ($12\,600 \pm 1100$ ppbv;⁴⁶).

The nontunnel VOC levels in Mecca ($21^\circ N$) were compared with VOCs measured using the same technique in two other cities at similar latitudes but different time frames, namely Karachi, Pakistan at $26^\circ N$ in January 1999 ($n = 50$;⁷) and Lahore, Pakistan at $31^\circ N$ in December 2012 ($n = 48$; unpublished data collected by our group) (Figure 5). The average nontunnel CO levels in Mecca both during and after Hajj (2230 ± 380 ppbv and 1770 ± 270 ppbv, respectively) were similar to Karachi (1600 ± 180 ppbv) and lower than Lahore, which is one of the world's most densely populated cities (4480 ± 610 ppbv). Other VOCs measured in Mecca (e.g., ethene, ethyne, benzene) also showed Hajj and non-Hajj averages that were lower than Lahore and similar to or lower than Karachi (Figure 5). By contrast, the gasoline evaporation tracer *i*-pentane was notable because its Mecca average both during and after Hajj (42 ± 17 ppbv and 55 ± 20 ppbv, respectively) was much higher than in Karachi (12.1 ± 1.6 ppbv) and similar to Lahore (44 ± 8 ppbv). The maximum *i*-pentane levels in Mecca during and after Hajj (806 and 851 ppbv, respectively) were much higher than in Karachi and even Lahore (90 and 222 ppbv, respectively). Likewise, the reactive butenes and pentenes that correlated well with *i*-pentane (see above) were also elevated in Mecca relative to Karachi, and similar to or higher than Lahore (Figure 5).

Together the above results show that (1) gasoline evaporation is a strong VOC source in Mecca that needs to be considered in emission reduction strategies, and (2) even without the presence of Hajj, levels of CO and VOCs in Mecca are already elevated and often similar to those in some of the world's major cities. Therefore, strategies to improve air quality in Saudi Arabia are appropriate at all times of the year.

Recommendations. More work is needed to quantify the spatial and temporal variations of ozone-forming VOCs in Saudi Arabia and to better characterize their sources, especially the composition of evaporative fuel sources including LPG and gasoline. However, the results reported here lead us to put forward the following initial recommendations.

(1). *Establish Realistic Emission Standards and Emission Inspections for Vehicles.* Currently there are no practical emission standards for vehicles in Saudi Arabia, and many private vehicles on the road are models from the 1970s. VOC emissions increase with vehicle age and low standards of maintenance, and most VOCs are emitted by a small percentage of the vehicle fleet.⁴⁷ Therefore, vehicle emissions inspection and maintenance programs could be used to identify and fix vehicles with the highest pollutant emissions.

(2). *Continue to Enhance the Public Transportation System.* Current efforts by the Saudi government to build a public mass transportation system, including trains that connect Mecca with the holy sites of Arafat, Muzdalifah and Mina, are important and will help to reduce the number of vehicles on the road.

(3). *Reduce VOC Emissions at Gas Stations and Strengthen Occupational Safety Measures.* Almost all gas stations in Saudi Arabia are full service stations, and workers are exposed to gasoline vapors for many hours each day. Similar to countries such as the U.S. and Canada, we recommend adding vapor recovery capability to the fuel pump hoses in Saudi Arabia (e.g., adding plastic seals to the fuel pump nozzles) in order to minimize both emissions of VOCs and exposure to them while vehicles are being refueled.

(4). *Implement Penalties for Idling.* Similar to many North American cities, drivers in Saudi Arabia could be subjected to fines if their engines are left idling for unreasonable periods of time.

(5). *Reduce the Exposure of Pedestrians and Others to Poor Air Quality in Tunnels.* This could be achieved by using separate tunnels for pedestrians and vehicles. In the meantime, existing tunnels could be modified by adding extra emergency exits and ventilation systems. We also recommend carefully monitoring the health of workers and police in tunnels, for example assigning a maximum number of working hours in tunnels based on exposure and risk assessment studies. Looking forward, we suggest a detailed study for remodeling existing tunnels and designing new tunnels, making health of the tunnel users a priority.

(6). *Identify and Reduce Emissions of Key Ozone Precursors.* Our analysis suggests that CO and alkenes strongly contribute to O₃ formation in Mecca. However, a full understanding of the oxidative environment in Mecca also requires concurrent measurements of NO_x coupled with modeling studies. Therefore, we recommend comprehensive air quality monitoring and modeling in future work, including simultaneous VOC and NO_x measurements.

Because the number of pilgrims is expected to continue to increase in the future, air quality problems and impacts on human health remain a concern in the Mecca area. In addition to the above recommendations, future air quality studies could perform detailed source sampling and use source apportionment techniques to better quantify specific source influences on air quality. Further, Mecca is a city of tunnels, and future research could further assess air quality in both vehicle and pedestrian tunnels. For example, in order to better assess short-term exposure of individuals who spend extended time in the tunnels—such as police, volunteers, security and shift-workers—air samples could be collected over 30 min and 1 h integration times.

■ ASSOCIATED CONTENT

■ Supporting Information

Sampling details and locations are given in Table S1 and Figure S1. Statistics for the measured VOCs are given in Table S2. Selected VOC correlations are shown in Figures S2–S5. Additional sampling and analytical details are given, and the potential influence of natural gas sources is discussed. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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